DETERMINING THE GELATION PROPERTIES OF PLASTICIZERS USING THE BRABENDER PLASTOGRAPH

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DETERMINING THE GELATION PROPERTIES OF PLASTICIZERS USING THE BRABENDER PLASTOGRAPH

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ABSTRACT. A new procedure for determining the gelation and stability properties of plasticizers, under conditions approximating real processing conditions, is described. The Brabender plastograph was used to estimate the gelation behavior of several platicized PVC mixtures. A characteristic curve for the bonding due to the viscosity of the melted material as a function of the time is given for a plasticized PVC mixture. The effect of various factors upon the gelation properties of PVC-plasticizer mixtures is illustrated.

The gelation and stability properties of plasticizers can /87* be determined under conditions approximating real processing conditions using a rotational rheometer. A rheometer of this type is the Brabender plastograph.

The Brabender plastograph operates on the principle of measuring the bonding time due to the resistance caused by the viscosity of the melted material when two worms rotate in opposite directions.

A given quantity of material is placed in a thermostatic tank, so that the tank is completely full. In this case, the material is mixed by two rotors with complex, geometrical shapes, which reproduce, on a reduced scale, the shape of the stirrers used in industrial mixers. The rotor speed can be regulated continuously by a reducer, which has a constant reduction ratio of 1 : 1.5. The drive rotor transmits the bond across a lever system to a recording device.

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* Numbers in the margins indicate pagination in the foreign text.

This apparatus was used for the first time by Schmidt [1] to estimate the gelation behavior of plasticized PVC mixtures, and was later widely copied.

The procedures for determining and interpreting the results differ from laboratory to laboratory.

A plasticized PVC mixture has the following rheological properties. At room temperature, the viscosity of the mixture is very low, since the polymer particles covered by the layer of plasticizer slide over each other. As the temperature increases, the gelation phenomenon becomes noticeable, along with an increase in the viscosity of the mixture.

The viscosity begins to decrease during the mixing process, after reaching a maximum followed by a great increase in temperature due to the friction, since the temperature drops as a result of the thermal exchange with the walls of the tank.

The viscosity of the mixture can remain constant for a brief period of time, and subsequently increases due to degradation phenomena caused by the cross-linking of the polymer chains.

All variations in viscosity are followed by a proportional variation in the bonding, which is recorded during the mixing process.

A characteristic curve (Figure 1) for the bonding variation with respect to time has the following features:

- maximum bond C_M
- equilibrium or constant bond C_c
- minimum bond C_m

Each of these values has a corresponding characteristic time value: T_M, T_c and T_m.

The works of Schmidt [1] indicate the use of a mixture of of two parts PVC and one part plasticizer, which is introduced

into a 300 g tank with a thermostat for temperatures from 25° to 100°C.

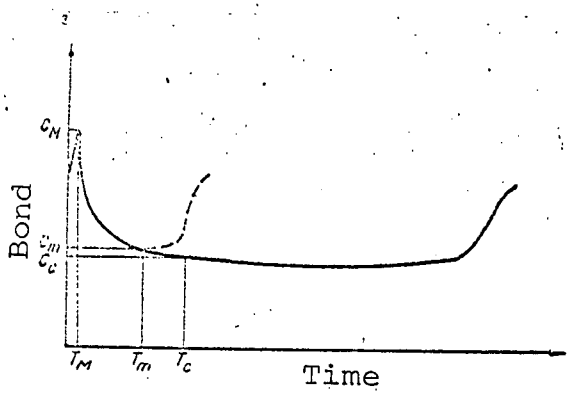

Figure 1. Characteristic curve for bonding as a function of time for a PVC-plasticizer mixture.

C_M - maximum bond; T_M - time of maximum bond; C_c - constant bond; T_c - time of constant bond; C_m - minimum bond; T_m - time of minimum bond; dotted line - minimum bond.

Assuming that the time need to reach a given bond, or the maximum bond is a measure of the gelation time, the gelation rate as a function of the temperature was investigated for mixtures made with different plasticizers.

Several researchists, working in the 100-180°C temperature range on mixtures of 30 parts PVC and 20 parts plasticizer, have suggested another procedure for determining the curves for the variation of the bonding with respect to time, assuming that the gelation capacity and the gelation time are given when a constant bond is attained [2].

In order to apply the results obtained with the Brabender plastograph to the industrial processing of plasticized PVC, it was suggested that certain limits be established for the maximum and equilibrium values of the bond and the corresponding

time values, which characterize the materials with good processability [3].

By studying the variation of the equilibrium bond as a function of the temperature, it was found that there is a "dissolving" temperature, which characterizes a given mixture. Below this temperature, the gelation is not far enough advanced, and above it, there is no change in the gelation state by the addition of more heat [4].

The value of the "dissolving" temperature depends on the the plasticizer composition and its content in the PVC mixture. The "dissolving" temperature of the PVC mixture increases as the quantity of the plasticizer in the mixture is increased.

A statistical study has shown the effect of various factors on the gelation properties of PVC-plasticizer mixtures [5] as follows.

- The maximum bond decreases as the temperature is increased and the sample in the tank is decreased. The maximum bond does not depend on the speed of rotation of the worm.
- The time necessary to reach the maximum bond increases as the quantity of the sample is increased.
- The equilibrium bond exhibits a dependency, which is analogous to the maximum bond when the temperature and quantity of the sample are varied.
- This bond reaches a maximum value as the plasticizer content is increased.
- The time needed to reach the constant bond, T_c, exhibits a minimum value for each combination of temperatures and quantities of samples, at approximately the same plasticizer concentration.

Determining the thermal stability of PVC-plasticizer mixtures was done by evaluating the time which elapsed before decomposition set in, which was manifested by a sudden increase in the bond at 160, 170 and 180°C [6].

Experimental Procedure

Investigations were carried out to developaa simple method /88 of determining plasticizer by determining the gelation and stability properties of PVC mixtures. In order to establish a dependence of these properties on the temperature, the method of temperature variation at a constant rate [4], which requires the use of a temperature programming system, was replaced by a method of determination at several different temperatures using a mixture with the same composition.

Thus, determinations were made with the tank wall kept at constant temperatures, namely 80 [1], 110 [2], 140 [7], 170 [6] and 190°C [6, 8]. All measurements were made on a 50 g mixture with the following composition [5]:

100 parts PVC-S K = 67;
50 parts plasticizer;
0.50 parts dibasic lead stearate.

The low-speed rotor ran at 50 rpm. The following groups of plasticizers were tested: phthalates: dioctyl phthalate (DOP), dinonyl phthalate (DNP), diisodecyl phthalate (DIDP); dioctyl sebaceate (DOS); diisooctyl adipate (DIOA); esters of trimellitic acid: octyl trimellitate (TMO), octyl-decyl trimellitate (TMOD); epoxydated soybean oil (USE) and polyadipates (PA_1, PA_2 and PA_3).

The preliminary investigations carried out at 80 and 110°C on DOP, PA_1 and PA_2 have yielded the following results. At 80°C, the mixing bond remains very small for a long period of time, increasing only slightly, and the material does not gelate. At 110°C, the maximum bond, C_M, for DOP is greater than the measurement range of the instrument (2 mkgf), and for PA_1 and PA_2, the time necessary to reach the maximum bond is too great (approximately 80 minutes) to allow evaluation within a convenient amount of time. For this reason, the measurements were continued at 140, 170 and 190°C.

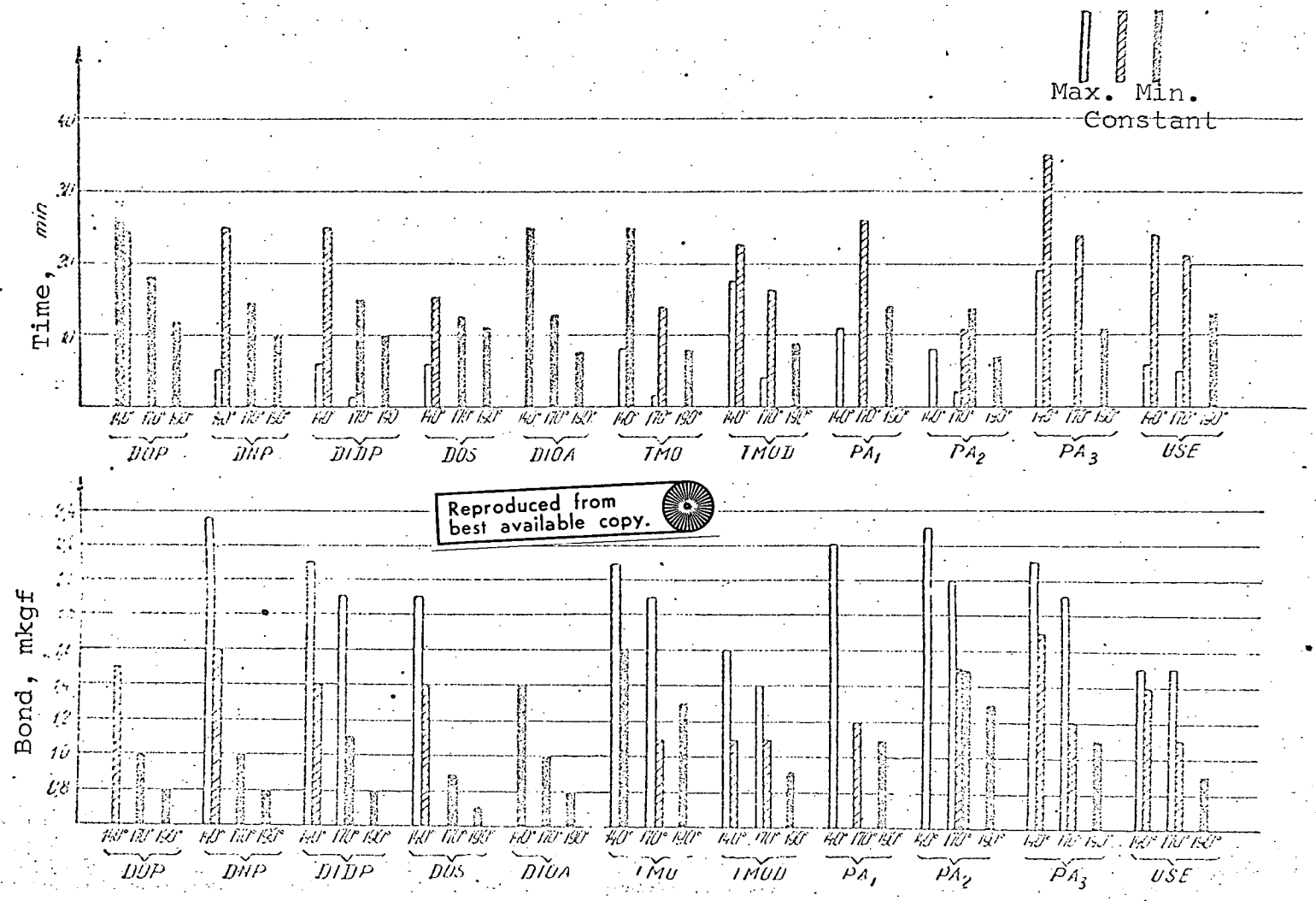

Figure 2. Characteristic values of the bonds and corresponding times.

At these temperatures, the plasticizers have different behaviors, which are manifested by the fact that the graphs recorded using the Brabender plastograph represent fragments of a typical curve as a function of the value of the characteristic times. The characteristic bonds and the corresponding times are given in Figure 2.

At 140°C, the plasticizers exhibit a maximum bond, with the exception of dioctyl phthalate and diisooctyl adipate, for which the time necessary to reach the maximum bond, T_M, was too short to be measured. If we assume, on the basis of the pertinent literature, that a small maximum bond time, T_M, characterizes a material which gelates rapidly and can be more easily processed in industrial installations, the following sequence of gelation rates can be found: DNP, DIDP, DOS, USE, TMO, PA_2, PA_1, TMOD, PA_3.

The highest gelation rate was obtained for DIOA and the phthalates; the gelation rate decreased as the alcohol chain increased from octyl to nonyl and decyl.

The same phenomenon has also been observed for the trimellitates. TMOD has a lower gelation rate than TMO.

In general, it was found that by increasing the molecular weight of the plasticizer, the gelation rate of the PVC mixture in which the plasticizer is used decreases.

The smaller the T_M (high gelation rate), the greater the mixing bond. A bond of this magnitude corresponds to a finished product with a high tensile strength and small elongation [9]. Two plasticizers do not observe this relationship, i.e. USE and TMOD, which, in addition to a high gelation rate, also have a relatively small maximum bond.

At 170°C, the time needed to reach the maximum bond decreases to such a degree that it cannot be determined in several cases.

The constant bond, which is determined at this temperature for most of the materials, depends primarily on the PVC molecular weight. The measurements carried out by the authors yielded values between 0.9 and 1.2 mkgf (except in the case of PA_2). The time needed to reach a constant bond depends on the rate at which the thermal equilibrium is reached, but it is determined very inaccurately because the bond tends asymptotically toward this value.

Some mixtures have such low stability, even at 170°C, that the decomposition, which is indicated by an increase in the mixing bond, can be measured within a reasonable amount of time, the results being exhibited as the minimum bond and its corresponding time.

At 190°C, all mixtures have a minimum bond. Thus, in this /89 way it is possible to estimate the stability of the mixture as a function of the time needed to reach the minimum bond.

For the plasticizers in question, the following sequence of thermal stabilities for the PVC mixture can be estimated as: PA_1, USE, DOP, DOS, PA_3, DNP, DIDP, TMOD, TMO, DIOA, PA_2.

No correlation has been established between the structure of the plasticizers studied and the stability of their mixtures with PVC.

From the results obtained, and the pertinent technical literature, it can be seen that the processability of certain plasticized PVC mixtures, with respect to gelation and stability, is determined primarily on the basis of the values for the maximum and minimum bonds and their corresponding times.

In addition, it might be pointed out that the working conditions used by the authors can be recommended for plasticizer evaluation since these conditions make it possible to differentiate

the plasticizers with respect to gelation and stability. Yet it is necessary to determine whether these conditions can be applied to other classes of plasticizers.

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